LOWER BOUNDS FOR EIGENVALUES*

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ABSTRACT

Various methods for the calculation of lower bounds for eigenvalues are examined, including those of Weinstein, Temple, Bazley and Fox, Gay, and Miller. It is shown how all of these can be derived in a unified manner by the projection technique. The alternate forms obtained for the Gay formula show how a considerably improved method can be readily obtained. Applied to the ground state of the helium atom with a simple screened hydrogenic trial function, this new method gives a lower bound closer to the true energy than the best upper bound obtained with this form of trial function. Possible routes to further improved methods are suggested.

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Although there exists a considerable literature[1] on the subject of lower bounds to eigenvalues, these methods have been relatively little used. The earlier methods all required the calculation of $\overline{H^2}$, H being the Hamiltonian. This is usually difficult. In addition, the lower bounds obtained have normally deviated from the true energy much more than does the upper bound $\bar{H}$.

The tremendous advantage of being able to calculate both upper and lower bounds and hence of endowing quantum mechanics with a genuine power of prediction has spurred the search for more practical and more efficient methods. In the last few years a number of promising new approaches have been opened up.[2] It is the purpose of this paper to show how several of these methods can be related to one another, and, in consequence to demonstrate a modified method of considerably improved accuracy.

The Expansion Method

The older formulas can all be derived by an elementary expansion method, as shown by Crawford and Stevenson.[3] The trial function ϕ is imagined to be expressed in terms of the set of true eigenfunctions ψ_n, i.e.

$$\phi = \Sigma c_n \psi_n, \quad \Sigma c_n^2 = 1. \tag{1}$$

One then writes

$$I = \int \phi\,(H - \alpha)^2\,\phi d\tau = \overline{H^2} - 2\alpha\bar{H} + \alpha^2$$

$$= \Sigma c_n^2\,(E_n - \alpha)^2 \geq (E_o - \alpha)^2 \tag{2}$$

if the constant α is chosen so that

$$(E_o - \alpha)^2 \leq (E_n - \alpha)^2 \tag{3}$$

the E_n being the true eigenvalues. The various different methods result if appropriate values are assigned to α. In particular Kato[4] has shown by a different argument, that when only $\overline{H^2}$, $\bar{H}$ and a lower bound, E_1^L, for

the first excited state are known, then the best lower bound for E_o is Temple's[5]

$$E_o \geq E_o^L = \frac{E_1^L \bar{H} - \overline{H^2}}{E_1^L - \bar{H}} \tag{4}$$

which can be derived above by giving α its maximum safe value

$$2\alpha = E_o^L + E_1^L \tag{5}$$

and solving* for E_o^L.

It is worth pointing out that Temple's formula can be modified to apply to discrete excited states as well as to the ground state. Further, although in practice it has generally given a worse approximation to the eigenvalue than does $\bar{H}$, this is not always true. In fact, in a special case, the exact eigenvalue can be obtained from an approximate trial function ϕ. This occurs when E_1 is exactly known and only c_o and c_1 appear in the expansion of ϕ. However, it may be empirically justified to get a better probable lower limit by averaging the Temple E_o^L with $\bar{H}$.

If no information regarding E_1 is available, Weinstein's[6] formula, which uses $\bar{H}$ for α, may be used, but if, in fact $\bar{H}$ is greater than $\frac{1}{2}(E_o + E_1)$, the result may not be a true lower limit to E_o. Ordinarily, Weinstein's formula is much less efficient than Temple's. It cannot be better than Temple and still be a guaranteed lower bound. Even a very rough value for E_1 can often give a Temple bound considerably better than the Weinstein bound. If the Weinstein lower bound is averaged with the

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*A better lower bound can of course be found by using the true value of E_o or a guess higher than E_o^L in the expression for α, but although calculations of this sort are found in the literature, they clearly beg the question. If one knows a better value of E_o^L in advance, there is no use in calculating a poorer value for this quantity.

upper bound $\bar{H}$, weighting the latter by the maximum amount which permits a guaranteed lower bound to result, the Temple value is obtained.

The Projection Method

In the atomic and molecular electronic problem, the interelectron repulsion contributes a term to the Hamiltonian which is always positive. The energy levels E_n^o calculated with the omission of this term are therefore always below the true energies E_n and provide well known but very poor lower bounds. The method of intermediate Hamiltonians[7] is to construct a series of Hamiltonian operators whose eigenvalues can be calculated and which lie between E_n^o and E_n. Further, by proceeding to later and later members of the series, the lower bounds can be improved to any extent desired.

One method of constructing intermediate Hamiltonians is the projection method.[7] Let

$$H = H^o + V, \qquad V > 0 \tag{6}$$

and choose a trial function ϕ, hopefully approximating a true eigenvalue ψ of H. Define a special projection operator P so that for any function χ in the domain of H,

$$P\chi = a\phi, \quad \chi = a\phi + \eta \tag{7}$$

where the coefficient a (which depends upon the function χ) is chosen to ensure the vanishing of the integral $\langle \eta V \phi \rangle$. Hence, from Eq. (7)

$$\langle \phi V \chi \rangle = a \langle \phi V \phi \rangle + \langle \phi V \eta \rangle \tag{8}$$

so

$$P\chi = a\phi = \langle \phi V \chi \rangle \langle \phi V \phi \rangle^{-1} \phi \tag{9}$$

The reason for this choice is that then

$$\langle \chi V \chi \rangle = \langle P\chi V P\chi \rangle + \langle \eta V \eta \rangle \geq \langle P\chi V P\chi \rangle = \langle \chi V P\chi \rangle \tag{10}$$

for any suitable χ. This is mathematically sufficient so that the eigenvalues E_n^L of the modified equation

$$(H^o + VP)\chi = E^L \chi \tag{11}$$

when properly ordered, satisfy

$$E_n^o \leq E_n^L \leq E_n \tag{12}$$

Further, a formal solution for the eigenfunction χ is

$$\chi = -(H^o - E^L)^{-1} VP\chi = -a(H^o - E^L)^{-1} V\phi \tag{13}$$

with $$\langle\phi V\phi\rangle a = \langle\phi V\chi\rangle$$

when $E^L \neq E_n^o$.

Further progress can be made[8] by choosing ϕ in terms of a new function such that

$$\phi = V^{-1} (H^o - E^L)\, \xi \tag{14}$$

Hence $$\chi = -a\xi \tag{15}$$

and the equation for $\underline{a}$ becomes

$$\langle \xi\, (H^o - E^L)\, V^{-1}\, (H^o - E^L)\, \xi\rangle\, a = -\langle \xi\, (H^o - E^L)\, \xi\rangle\, a \tag{16}$$

which has a non-vanishing solution only if

$$\langle \xi\, f\, (E^L)\, \xi\rangle = 0 \tag{17}$$

where $$f\,(E^L) = (H^o - E^L)\, V^{-1}\, (H^o - E^L) + (H^o - E^L) \tag{18}$$

Provided that Eq. (17) has a real solution and that $V>0$, E^L will be a lower bound to some eigenvalue of H. In particular,[8] since $E_n^o \leq E_n^L \leq E_n$, if E^L is below E_1^o it cannot be a lower bound for E_1 and hence must be a lower bound for E_o.

The trial function ξ can be in the form of a linear combination of some finite set of basis functions $\{\mu_n\}$ and the coefficients can be varied to maximize E^L. With $dE^L = 0$, this leads to

$$\Sigma c_n \langle \mu_n\, f\, (E^L)\, \mu_k\rangle = 0. \tag{19}$$

and hence to the finite secular equation

$$\det\, |\, \langle \mu_n\, f\, (E^L)\, \mu_k\rangle\, | = 0 \tag{20}$$

The typical element can be written in the expanded form,[8] from Eq. (18)

$$(V^{-1})_{nk} (E^L)^2 - (H^oV^{-1} + V^{-1}H^o + I)_{nk} E^L + (H^oV^{-1}H^o + H^o)_{nk} = 0 \quad (21)$$

where $$(V^{-1})_{nk} = \langle u_n V^{-1} u_k \rangle \text{ etc.}$$

Another form can be obtained from Eq. (13) by the substitution $\phi = V^{-1}\zeta$ or $\xi = (H^o - E^L)^{-1}\zeta$ in Eq. (16). This yields

$$\langle \zeta \mid V^{-1} + (H^o - E^L)^{-1} \mid \zeta \rangle = 0 \quad (22)$$

If ζ is expressed as a finite linear combination of eigenfunctions for H^o, i.e. as

$$\zeta = \sum_o^N a_s \psi_s^o \quad (23)$$

the associated finite secular equation[9] is

$$\left| (V^{-1})_{st} + \delta_{st} (E_s^o - E^L)^{-1} \right| = 0 \quad (24)$$

or

$$\left| (V^{-1})_{st}^{-1} + \delta_{st} (E_s^o - E^L) \right| = 0 \quad (25)$$

The form for $f(E^L)$ given in Eq. (18) can be usefully rewritten by replacing H^o by H-V, so that

$$f(E^L) = (H - E^L) V^{-1} (H - E^L) - (H - E^L) \quad (26)$$

This form shows that if $\xi = \psi_n$, an exact eigenfunction of H, then $E^L = E_n$ is a solution, because of the factor $H-E^L$. It further leads to the form, for normalized ξ,

$$E^L = \bar{H} - \int [(H - E^L)\ \xi]^2\ V^{-1}\ d\tau \quad (27)$$

Clearly V is not in principle limited to the interelectron repulsion. The method of proof required that V be positive definite and that E_1^o of H^o = H-V be greater than E^L. Otherwise V^{-1} is quite unrestricted. In practice the choice is limited by the problem of evaluating the integral and the requirement of determining that $E_1^o > E^L$, but it is possible to consider desirable qualities for V. Thus, for maximum E^L, V^{-1} should be small; i.e. V large, where $[(H - E^L)\ \xi]^2$ is large. At the same time, V should be small where ψ_1^o, the first excited state for H-V, is large, so as to keep $E_1^o > E^L$.

The simplest choice for V is a constant A. The maximum value for A is set by

$$E_1^o = E_1 - A \geq E_o^L \tag{28}$$

or

$$A = E_1^L - E_o^L \tag{29}$$

where E_1^L is a lower limit for the first excited state of H. This choice leads to

$$f(E^L) = (H - E_o^L)(H - E_1^L) \tag{30}$$

or

$$E_o^L = (E_1^L \bar{H} - \overline{H^2}) / (E_1^L - \bar{H}) \tag{31}$$

which is Temple's formula[4], Eq. (14). Hence all the older formulas can be derived from the projection technique for intermediate Hamiltonians.

Improved Formulas

Eq. (21) has been applied[8] to the ground state of helium with various trial functions of the Hylleraas type and was found to give better results than Temple's formula. However, when it is realized via Eq. (27) that V^{-1} is merely a weight factor, a considerable further improvement is easily obtained.

One way is to replace $V = 1/r_{12}$ by C/r_{12} where C is a suitably chosen constant greater than one. For a sufficiently good trial function ϕ at least, a higher (better) lower bound will be obtained by increasing C. However, C cannot be made too large or the result will no longer be a lower bound. A sufficient condition is that C be kept small enough so that the energy E_1^x of the first excited singlet state of the operator

$$H^x = H - C/r_{12} = H^o - (C-1)/r_{12} \tag{32}$$

is greater than E_o^L calculated with the given C. Since C/r_{12} is a positive operator, if the calculated E^L were really a lower limit, not to the ground state, but to the first excited singlet state of helium, then

this E^L would have to be greater than E_1^x defined above. If $E^L < E_1^x$, it must be also less than E_o, as desired.

For helium, accurate calculations are available via perturbation theory[10] for the $1s2s\ ^1S$ state, the separate perturbation terms $\epsilon^o\ \epsilon'\ \epsilon''\ \ldots$ can be inserted in the expansion

$$E_1^x = \epsilon^o - (C-1)\,\epsilon' + (C-1)^2\,\epsilon'' - (C-1)^3\,\epsilon''' \qquad (33)$$

to calculate a very good number for E_1^x as a function of C. Thus for $E_1^x = -2.903$, $C \doteq 1.73$, a safe value. Then Eq. (26) (or its equivalent Eq. (27)) is solved for E^L using $V = C/r_{12}$. With the simple screened hydrogenlike trial function

$$\phi = N\, e^{-Z'(r_1 + r_2)} \qquad (34)$$

the value $E^L = -2.947$ atomic units is obtained which is below the presumably correct energy (-2.9037) by 0.043 units.* This can be compared with the error .056 in the best upper bound for this form of function (which is obtained with a different value of Z'). Presumably the lower bounds with more complicated trial functions could be considerably improved by this means also, with no greater labor than required with $V = 1/r_{12}$.

Still another improved form can be obtained by using, instead of V,

$$V = E^o_{\ell+1} - E^L_o + V \qquad (35)$$

in Eq. (26) and

$$\phi = \sum_{n=0}^{\ell} c_n\, \psi^o_n\ . \qquad (36)$$

Here E^o and ψ^o refer to the problem with Hamiltonian H-V. The secular equation will have the form

$$\det \left| \delta_{ij}\,(E^o_{\ell+1} - E^o_i)^{-1} - \left\langle \psi^o_i\,(E^o_{\ell+1} - E^L + V)^{-1}\,\psi^o_j \right\rangle \right| = 0 \qquad (37)$$

This equation was derived by Miller[11] in a different way which has the advantage of releasing the restriction that V be positive definite. It gave good results[11] for excited states of helium.

*C = 1.80 was used.

Conclusion

The considerations above show that steady progress has been made in developing lower bound methods of improving efficiency. Further progress can be expected. Thus the form of V can surely be chosen so as to meet the requirements discussed above better than does $1/r_{12}$.

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